Supporting Information

Potassium Difluorophosphate as an Electrolyte Additive for Potassium Ion Batteries

Huan Yang,[a] *Chih-Yao Chen,*[b] *Jinkwang Hwang,*[a] *Keigo Kubota,*[b]

Kazuhiko Matsumoto,[a, b, c,*] *Rika Hagiwara*[a, b, c]

[a] Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

[b] AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory (ChEM-OIL), National Institute of Advanced Industrial Science and Technology (AIST), Sakyo-ku, Kyoto 606-8501, Japan

[c] Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8510, Japan

[*]Corresponding author:

E-mail: k-matsumoto@energy.kyoto-u.ac.jp

Table S1. Fitting results of the EIS data for the K/K symmetric cells with 0.5 M KPF_6-EC/DEC electrolytes containing different amounts of KDFP or FEC.[a]

Additives, EIS component		1 h	12 h	1 day	3 day	5 day
0 wt% KDFP	R_{bulk} / Ω	9.49	36.65	41.96	63.24	114.9
	R_{int} / Ω	6175	7331	8061	11853	13914
	C.F. / Hz	7.99	5.39	5.56	2.46	2.60
	Q / F $s^{\alpha-1}$	6.01×10^{-6}	6.04×10^{-6}	5.94×10^{-6}	6.01×10^{-6}	6.51×10^{-6}
	α	0.899	0.907	0.909	0.910	0.899
0.1 wt% KDFP	R_{bulk} / Ω	10.48	36.52	44.55	82.40	102.2
	R_{int} / Ω	2875	4062	5023	7585	8636
	C.F. / Hz	18.38	11.83	11.83	5.69	5.69
	Q / F $s^{\alpha-1}$	5.10×10^{-6}	5.52×10^{-6}	5.43×10^{-6}	5.24×10^{-6}	5.21×10^{-6}
	α	0.840	0.881	0.883	0.886	0.886
0.2 wt% KDFP	R_{bulk} / Ω	6.707	22.31	32.38	67.00	103.79
	R_{int} / Ω	1 794	3 077	3 128	4 831	5 424
	C.F. / Hz	25.97	11.84	11.84	7.99	7.99
	Q / F $s^{\alpha-1}$	6.27×10^{-6}	7.445×10^{-6}	7.13×10^{-6}	7.976×10^{-6}	7.195×10^{-6}
	α	0.904	0.881	0.887	0.861	0.881
0.3 wt% FEC	R_{bulk} / Ω	23.63	36.21	82.34	107.96	145.64
	R_{int} / Ω	17909	40580	77062	181307	203896
	C.F. / Hz	2.46	0.76	0.51	0.17	0.17
	Q / F $s^{\alpha-1}$	5.104×10^{-6}	5.242×10^{-6}	4.636×10^{-6}	4.581×10^{-6}	4.298×10^{-6}
	α	0.880	0.861	0.869	0.852	0.864
3 wt% FEC	R_{bulk} / Ω	19.01	64.38	79.69	108.4	208.6
	R_{int} / Ω	16246	40041	66 449	179735	223455
	C.F. / Hz	2.60	1.12	0.51	0.16	0.11
	Q / F $s^{\alpha-1}$	4.994×10^{-6}	5.039×10^{-6}	4.722×10^{-6}	4.249×10^{-6}	4.028×10^{-6}
	α	0.893	0.842	0.883	0.840	0.852

[a] *C.F.*, Q, and α denote characteristic frequency, CPE parameter, and CPE exponent, respectively.

Table S2. The peak positions (unit: V) in the d*Q*/d*V* plots of the K/graphite cells in 0.5 M KPF_6-EC/DEC with different additives during the first charge and discharge processes. See Figures 4 and S10 for the d*Q*/d*V* plots.

Additive	SEI formation	Charge			Discharge		
		Potassiation			Depotassiation		
		KC_{36}	KC_{24}	KC_8	KC_8	KC_{24}	KC_{36}
Additive-free	0.295	0.264	0.201	0.151	0.279	0.367	0.485
0.1 wt% KDFP	0.351	0.263	0.228	0.172	0.265	0.352	0.464
0.2 wt% KDFP	0.358	0.280	0.241	0.184	0.261	0.350	0.462
0.3 wt% FEC	1.197	0.227	0.140	0.068	0.438	0.583	0.739
3 wt% FEC	1.245	0.035	0.079	0.136	0.410	0.518	0.680

Table S3. Coulombic efficiencies (%) of the K/graphite cells with 0.5 M KPF_6-EC/DEC electrolytes containing different amounts of KDFP or FEC. The charge-discharge rate is C/20.

Cycle number	KDFP			FEC	
	0 wt%	0.1 wt%	0.2 wt%	0.3 wt%	3 wt%
1st	84.5	86.1	86.9	79.2	65.3
2nd	95.9	98.2	99.8	96.0	88.7
3rd	96.9	99.1	99.8	99.2	92.8

Table S4. Binding energy (eV) and assignments of the XPS data on the graphite and in 0.5 M KPF_6-EC/DEC electrolytes containing different amounts of KDFP.

	K2p	F1s	C1s	O1s	P2p
Graphite electrode					
0 wt% KDFP	295.2 (KF, $2p_{3/2}$) 292.5 (KF, $2p_{1/2}$)	687.5 (CF_x, PF_x) 683.6 (KF)	289.5 (CO_3^{2-}) 288.1 (C=O) 286.4 (C–O) 284.7 (C–C) 282.6 (K–C)	533.3 (C–O) 531.4 (C=O) 529.4 (K–O)	137.6 (K_xPF_y)
0.2 wt% KDFP	295.4 (KF, $2p_{3/2}$) 292.6 (KF, $2p_{1/2}$)	687.6 (CF_x, PF_x) 683.6 (KF)	289.5 (CO_3^{2-}) 288.0 (C=O) 286.4 (C–O) 284.6 (C–C) 282.9 (K–C)	533.6 (C–O) 531.7 (C=O) 528.8 (K–O)	137.7 (K_xPF_y) 133.7 (PO_x, Phosphate)
Pristine			290.9 (CF_x, PVDF) 287.2 (C=O) 286.1 (C–O) 285.3 (C, sp^3) 284.4 (C, sp^2)	533.6 (C–O) 532.1 (C=O)	
K metal					
0 wt% KDFP		687.5 (CF_x, PF_x)			
2 wt% KDFP		687.4 (CF_x, PF_x) 683.2 (KF)			

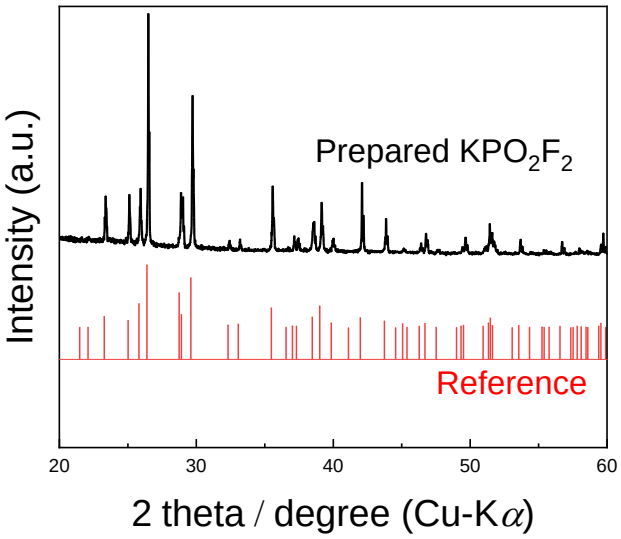

Figure S1. X-ray diffraction pattern of the prepared KDFP. The reference pattern of $K[PO_2F_2]$ created from the single crystal X-ray diffraction data[1] is also shown for comparison.

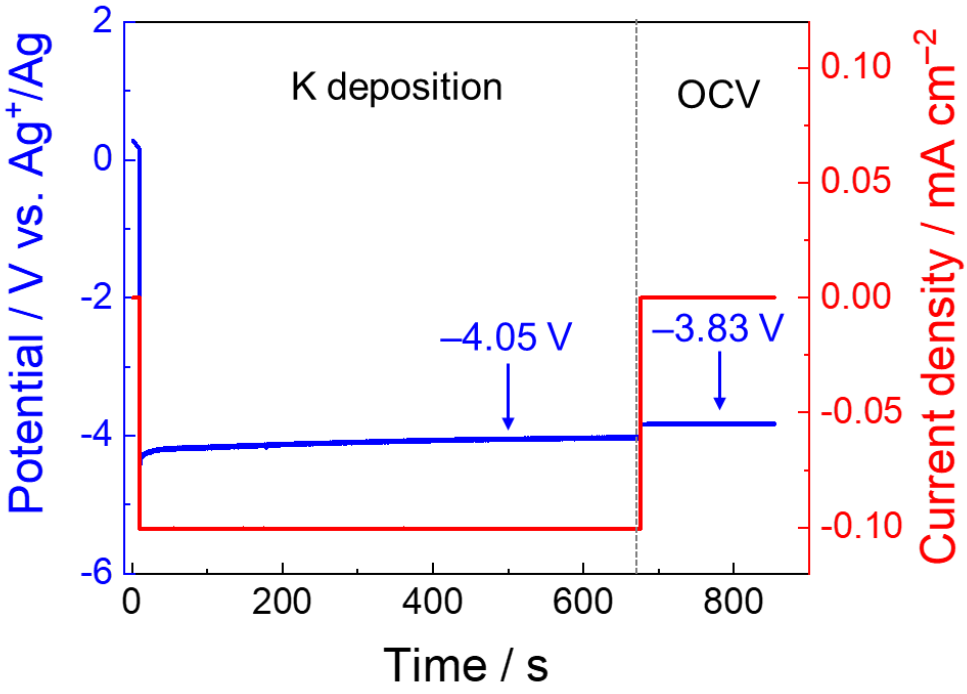

Figure S2. The voltage profile of K deposition/dissolution in 0.5 M KPF_6-EC/DEC on the Al working electrode (area: 0.25 cm^{-2}) with the Ag^+/Ag reference electrode and Pt counter electrode in a three-electrode cell. The K^+/K equilibrium potential in 0.5 M KPF_6-EC/DEC is determined to be –3.83 V vs. Ag^+/Ag by an open circuit potential (OCP) measurement after galvanostatic K metal deposition at 0.1 mA cm^{-2} in a three-electrode cell.

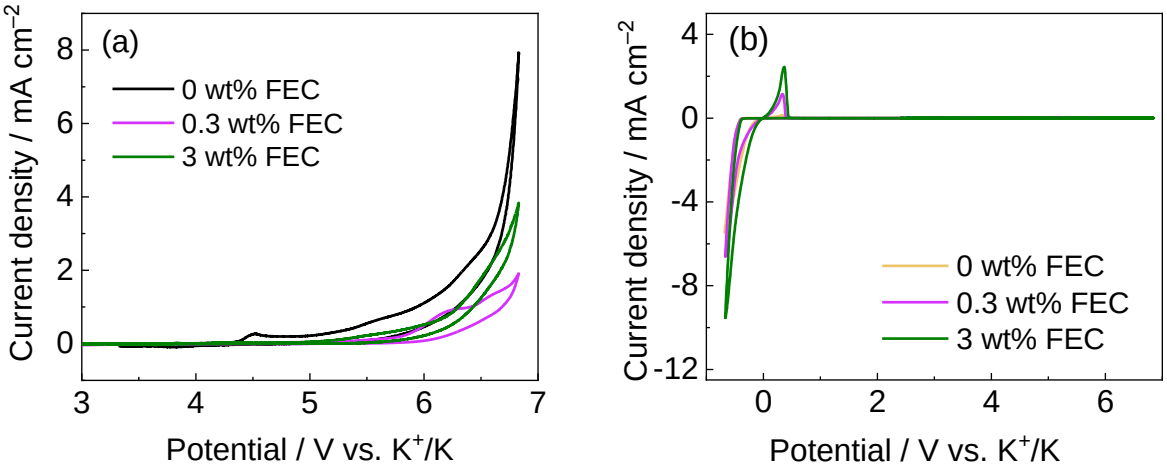

Figure S3. Cyclic voltammograms of (a) Pt (at anodic side) and (b) Al (at anodic and cathodic sides) plate electrodes in 0.5 M KPF_6-EC/DEC with 0.3 wt% KDFP, 0.3 wt% and 3 wt% FEC. Scan rate: 5 mV s^{-1}.

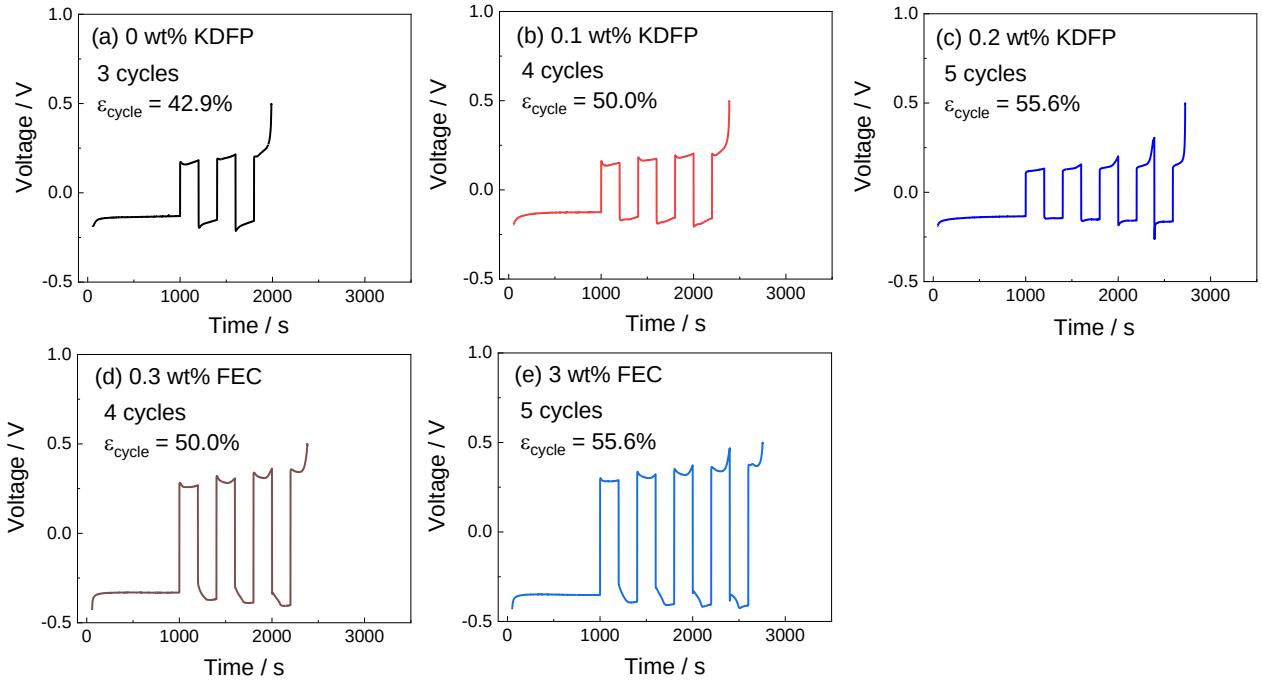

Figure S4. Voltage profiles during K deposition/dissolution in 0.5 M KPF_6-EC/DEC with (a) 0 wt% KDFP, (b) 0.1 wt% KDFP, (c) 0.2 wt% KDFP, (d) 0.3 wt% FEC, and (e) 3 wt% FEC at 25 °C. The working and counter electrodes were Cu and K metal plates, respectively. K metal (0.1 C cm^{-2}) was pre-deposited on the Cu plate, followed by repeated dissolution and deposition at a capacity of 0.02 C cm^{-2} until the electrode potential reached 0.5 V vs. K^+/K during dissolution. The current density was ± 0.1 mA cm^{-2} for all the tests.

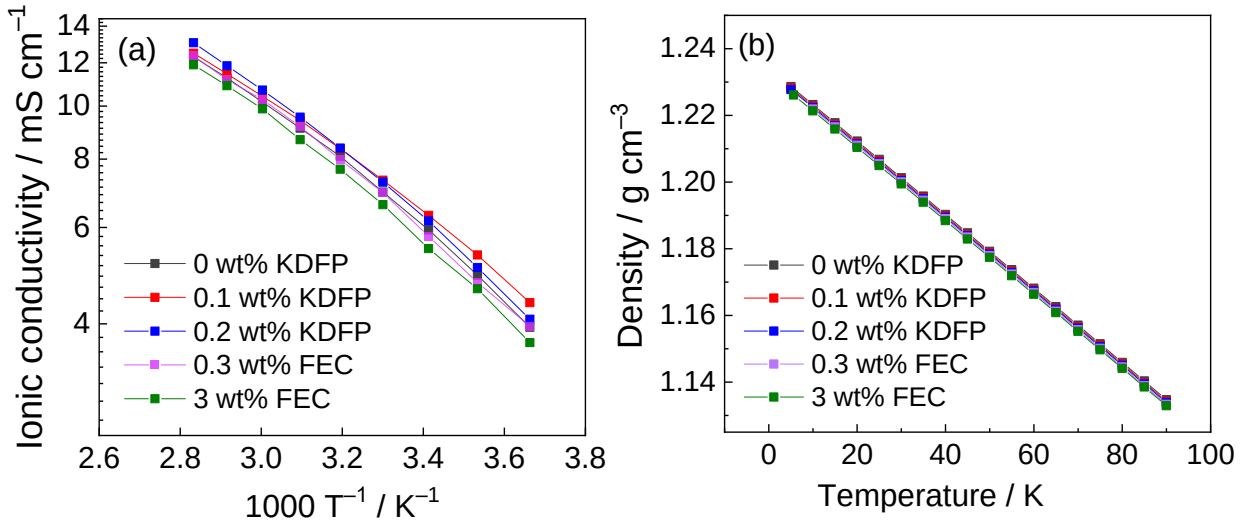

Figure S5. (a) Arrhenius plots of ionic conductivities and (b) densities of 0.5 M KPF_6-EC/DEC (1:1, v:v) without and with KDFP or FEC additives in the temperature range between 0 and 90 °C.

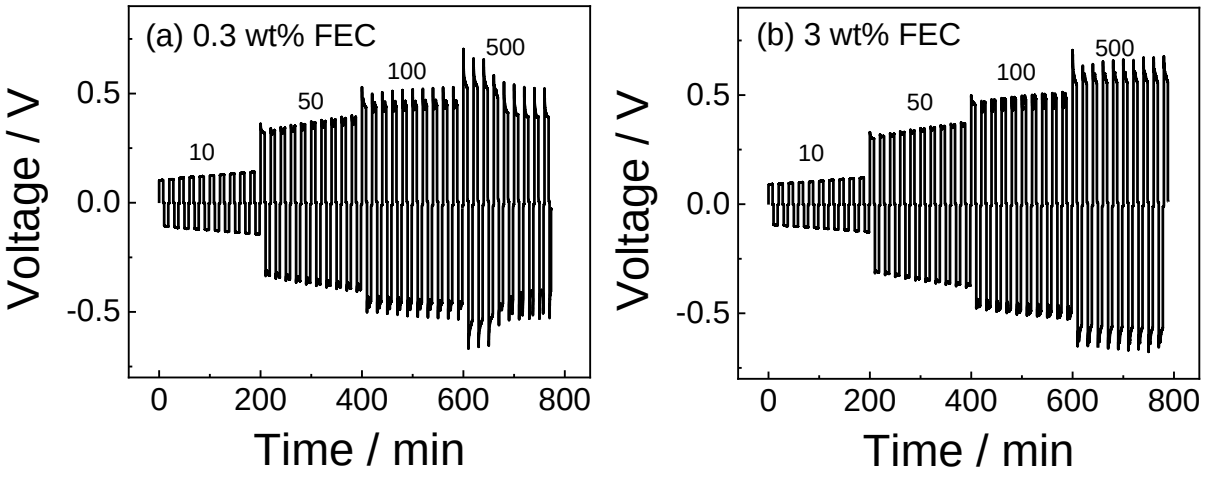

Figure S6. Voltage profiles of the K/K symmetrical cells during galvanostatic K metal deposition/dissolution in 0.5 M KPF_6-EC/DEC with (a) 0.3 wt% and (b) 3 wt% FEC additives at 25 °C. The numbers shown in each panel denote current densities in $\mu A \cdot cm^{-2}$.

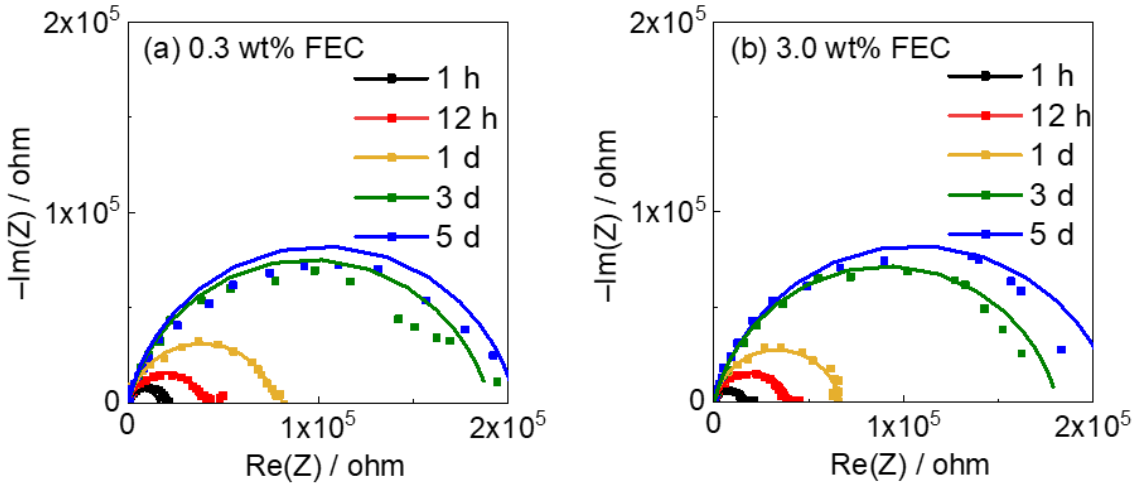

Figure S7. Nyquist plots and fitting lines of the K/K symmetric cells with 0.5 M KPF_6-EC/DEC with (a) 0.3 wt% and (c) 3 wt% FEC additives at 25 °C in the frequency range of 100 kHz−10 mHz. AC amplitude: 10 mV.

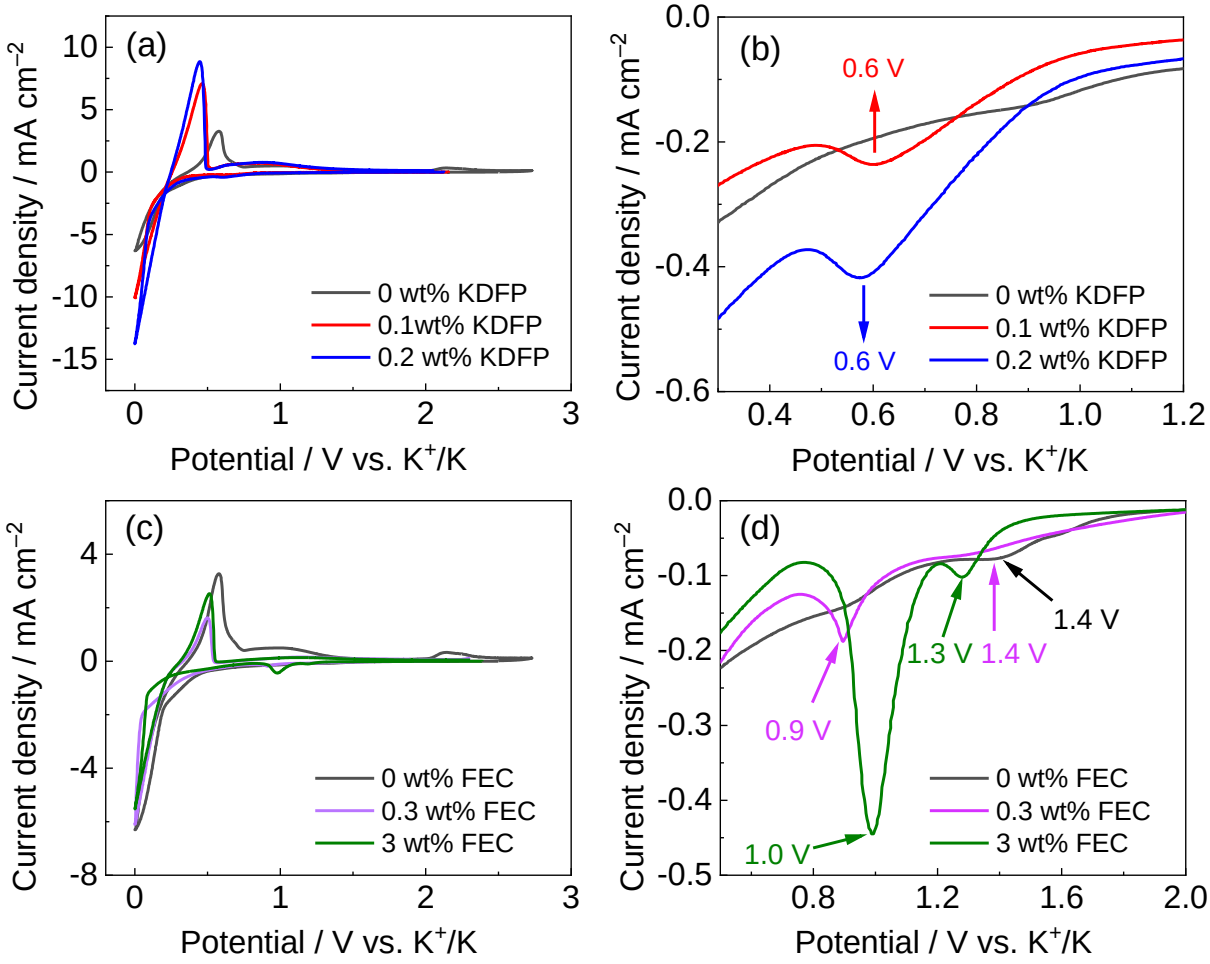

Figure S8. Cyclic voltammograms of graphite electrodes in 0.5 M KPF_6-EC/DEC with (a) 0 wt%, 0.1 wt%, and 0.2 wt% KFDP, (c) 0 wt% FEC, 0.3 wt% FEC and 3 wt% FEC additives at 25 °C. (b, d) Magnified figures of (a) and (c). Scan rate: 5 mV s^{-1}. Pt counter and Ag^+/Ag reference electrodes were used. The potential was converted to that against the K^+/K reference.

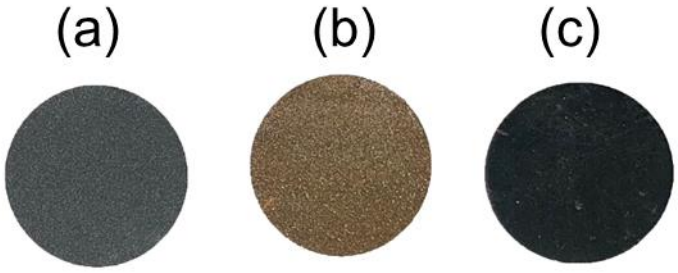

Figure S9. Photos of (a) as-prepared, (b) fully potassiated, and (c) fully depotassiated graphite electrodes obtained in 0.5 M KPF_6-EC/DEC by galvanostatic charge-discharge tests. C-rate: C/20 (1C = 279 mA g^{-1}).

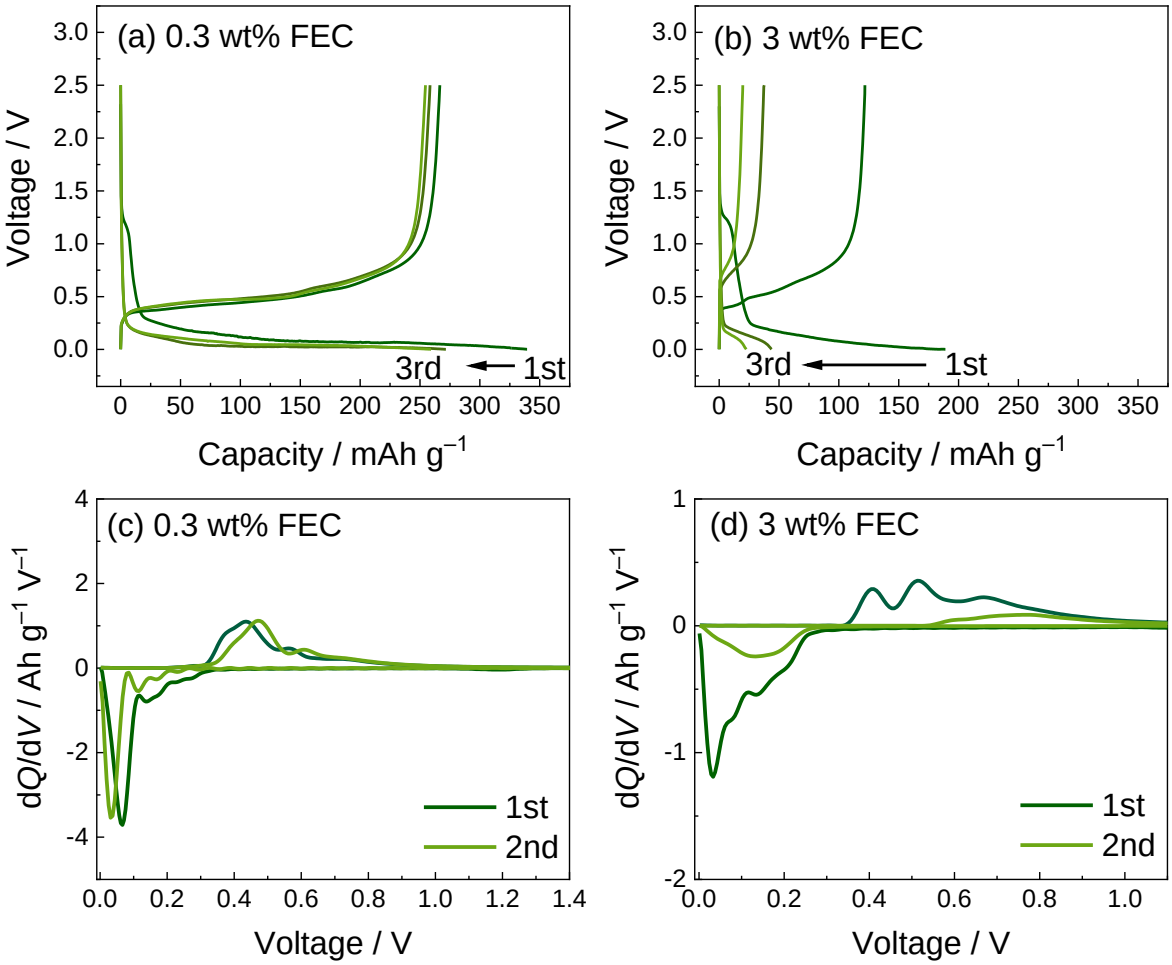

Figure. S10. Charge-discharge curves of the K/graphite cells in 0.5 M KPF_6-EC/DEC electrolytes with (a) 0.3 wt% and (b) 3 wt% FEC. C-rate: C/20 (1C = 279 mA g^{-1}). The corresponding differential capacity vs. voltage (d*Q*/d*V*) plots of the first two charge-discharge cycles are shown in (c) and (d).

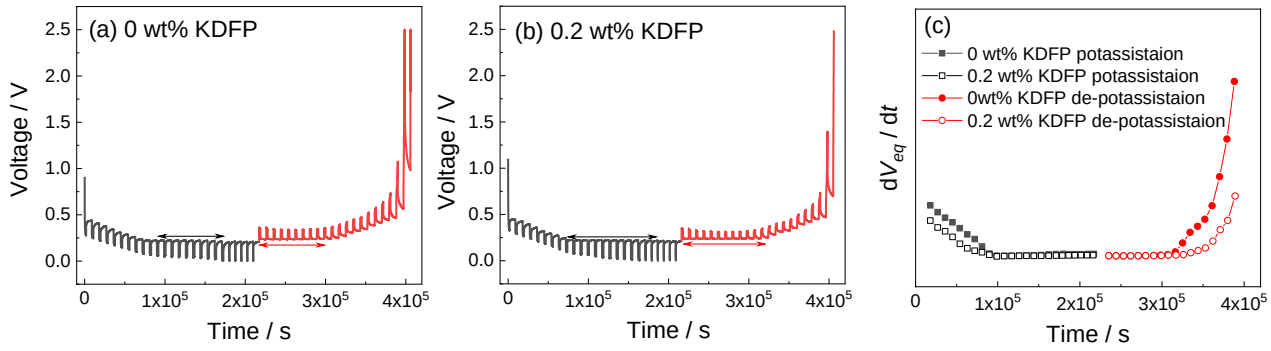

Figure S11. Galvanostatic intermittent titration technique (GITT) curves of graphite electrodes in 0.5 M KPF_6-EC/DEC with (a) 0 wt% and (b) 0.2 wt% KDFP. (c) Quasi-equilibrium voltage variation depends on the time change during charge-discharge process. GITT was measured by applying a constant rate of C/20 for 30 min followed by voltage relaxation for 2 h.

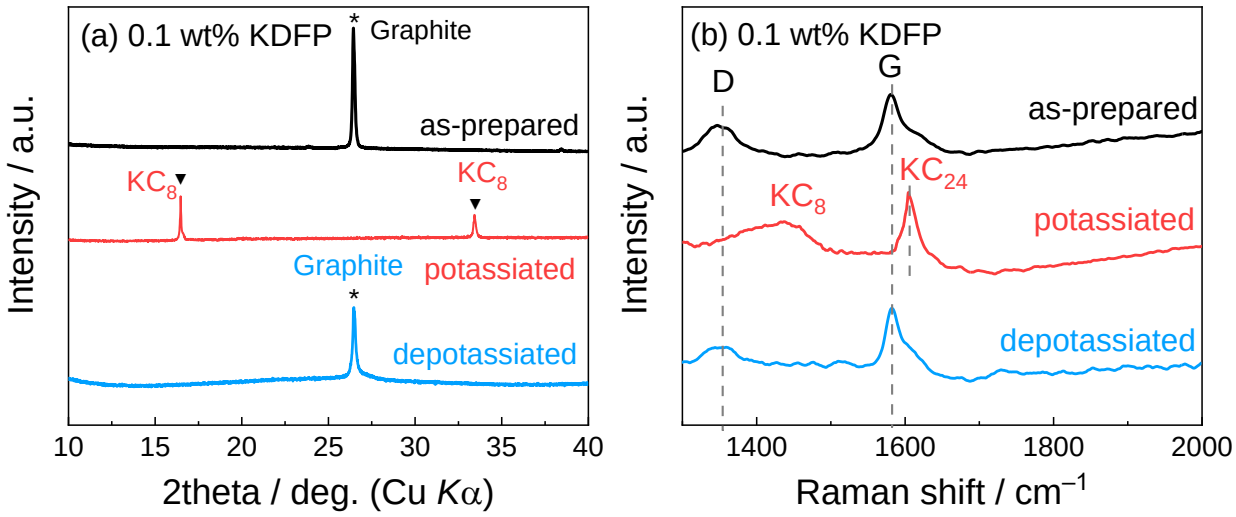

Figure S12. (a) *Ex-situ* XRD patterns and (b) Raman spectra of graphite electrodes at the pristine (black), fully potassiated (red), and fully depotassiated (blue) states recovered from 0.5 M KPF_6-EC/DEC with 0.1 wt% KDFP.

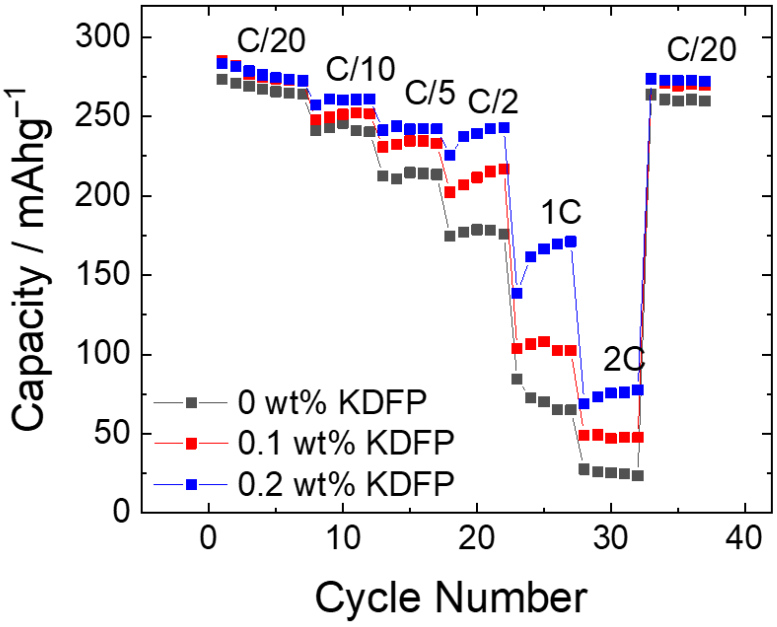

Figure S13. Rate capability of the K/graphite cells with 0.5 M KPF_6-EC/DEC electrolytes containing different amounts of KDFP at 25 °C. Rate: C/20 to 2C. Cut-off voltages: 0.001–2.5 V

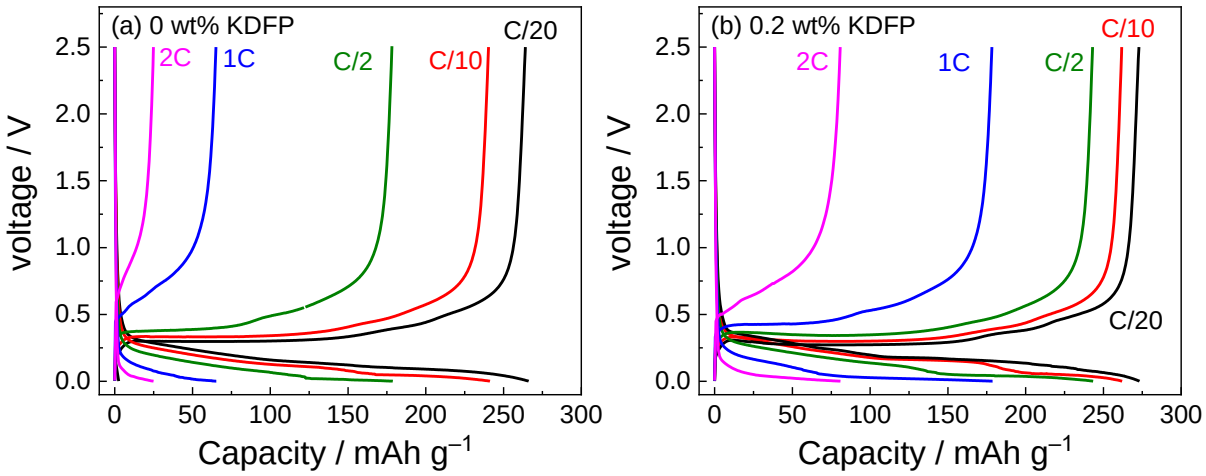

Figure S14. Charge-discharge curves of the K/graphite cells in 0.5 M KPF_6-EC/DEC with (a) 0 wt% and (b) 0.2 wt% KDFP during rate capability tests from C/20 to 2C at 25 °C. Cut-off voltages: 0.001–2.5 V.

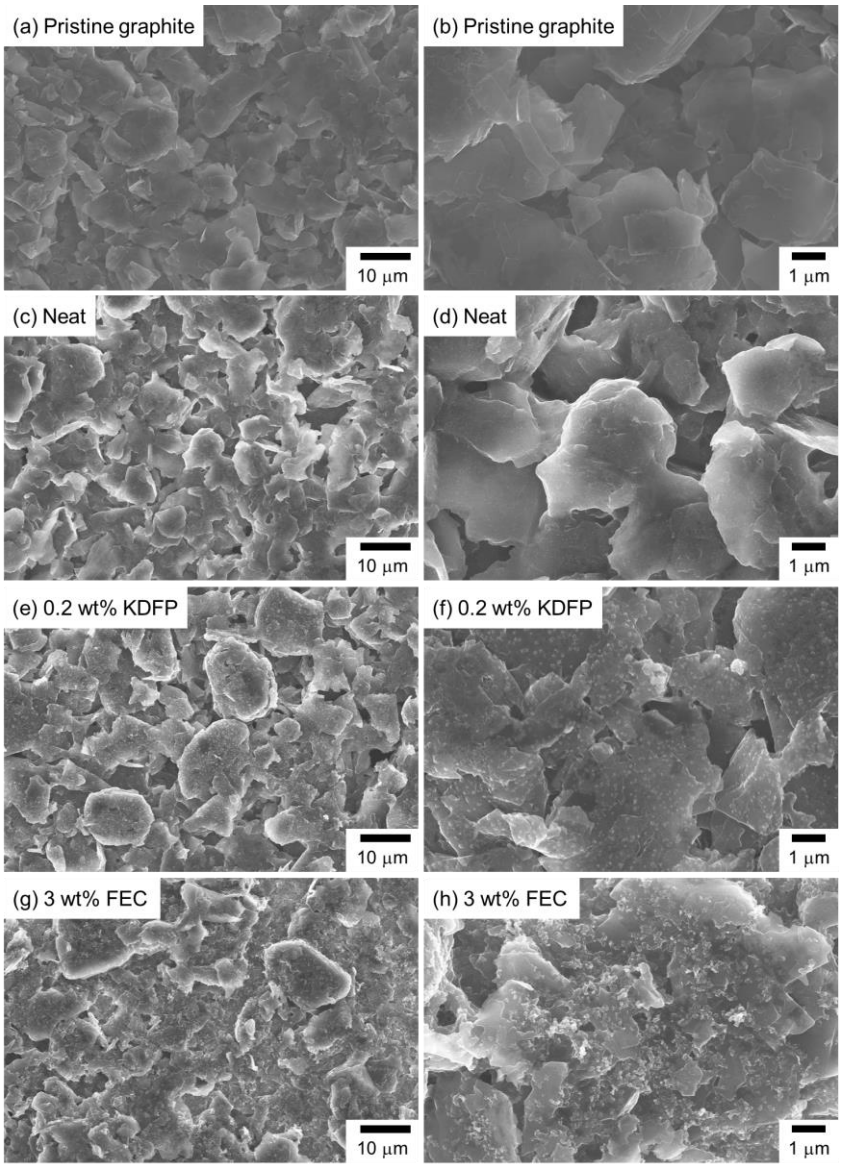

Figure S15. SEM images of (a, b) the pristine graphite electrode and the graphite electrodes after cycling in (c, d) 0 wt% additive (neat) (400 cycles), (e, f) 0.2 wt% KDFP (400 cycles), and (g, h) 3 wt% FEC (3 cycles). C-rate: C/3. Cut-off voltage: 0.001–2.5 V.

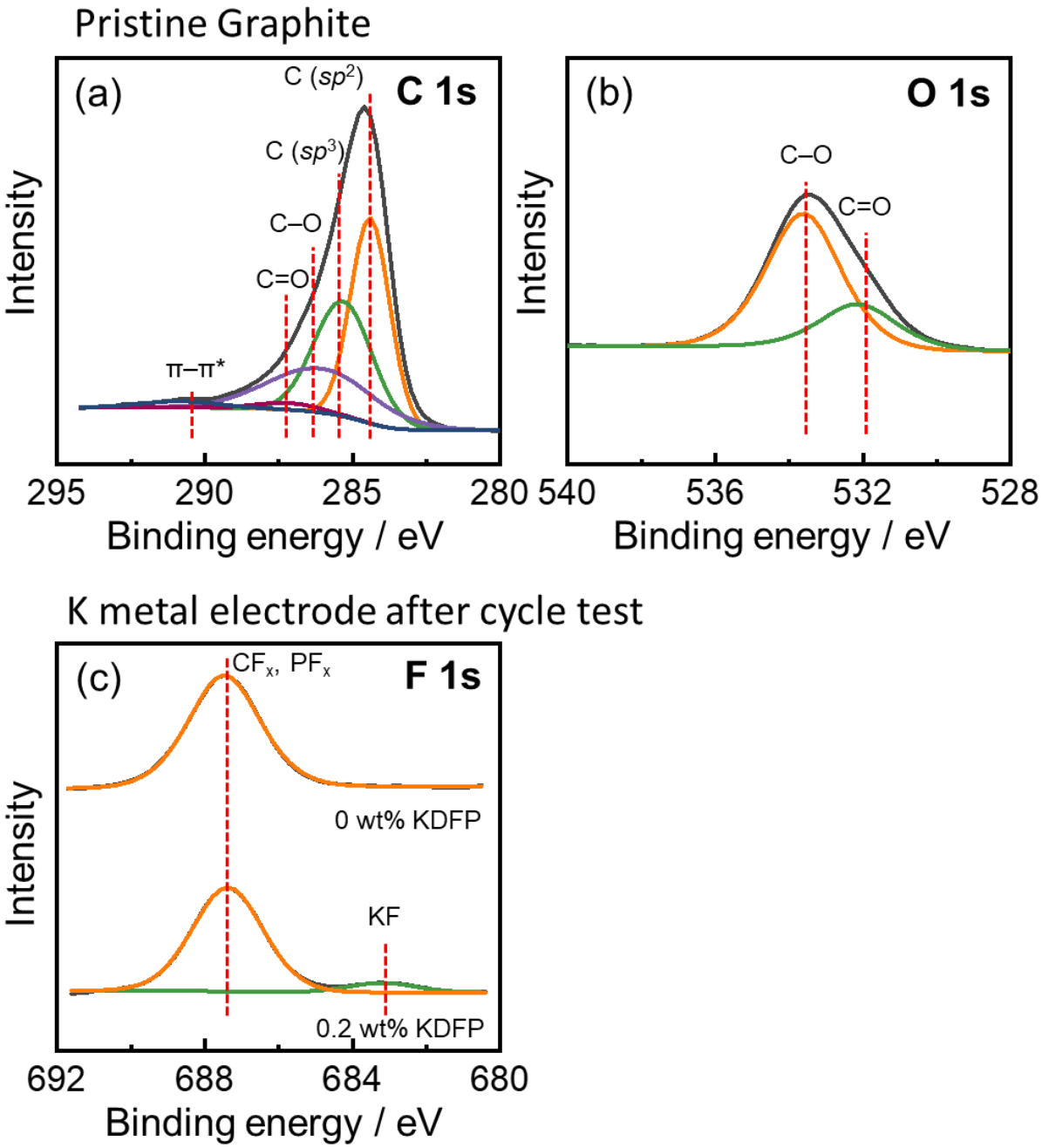

Figure S16. X-ray photoelectron spectra of the pristine graphite electrode ((a) C 1s and (b) O 1s) and (c) K metal counter electrode (F 1s) after 400 cycles using 0.5 M KPF_6 EC/DEC with and without KDFP additive.

References

[1] R. Harrison, R. Thompson,and J. Trotter, The structure of potassium difluorophosphate. *J. Chem. Soc. A* **1966**, 1775-1780.